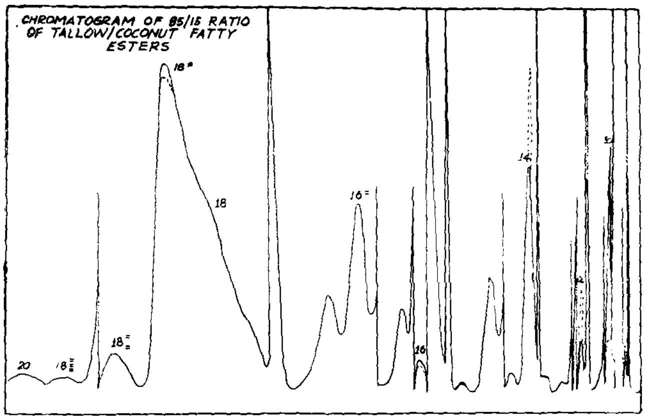

FIG. 4. Chromatogram of 85/15 ratio of tallow/coconut fatty esters with 75/25 ratio superimposed.

compared with a standard pattern and the closest one selected. Confirmation may be obtained by running the unknown sample and a standard mix on the same chromatogram using different colored inks.

Summary

1) In tallow-coconut soapstocks vapor-phase chromatographic techniques are superior in accuracy and less time-consuming than conventional physical-chemical methods.

2) For stocks containing other than tallow and coconut base, or where partial hydrogenation has been carried out, vapor-phase chromatography gives a more complete picture.

3) Vapor-phase chromatography gives indications of the source and/or prior treatment of a given stock.

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Sodium Alkyl *a*-Sulfopelargonates, $C_7H_{15}CH(SO_3Na)CO_2R$. Wetting and Related Properties[1]

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A series of sodium alkyl α-sulfopelargonates prepared from sodium α-sulfopelargonic acid and alcohols of from 2 to 12 carbon atoms were examined for surface active properties. Esters with the hydrophilic portion in the middle of the molecule, as in sodium hexyl, heptyl, octyl, capryl (or 2-octyl) and 2-ethylhexyl α-sulfopelargonate were very efficient wetting agents with good foaming properties and a c.m.c. of from 2 to 7 millimoles per liter. The presence of the α-sulfo group inhibits hydrolysis of the ester linkage, apparently by steric hindrance. Sodium capryl α-sulfopelargonate, an ester of a secondary alcohol, was particularly stable to acid and alkaline hydrolysis. The esters are easily soluble in water, organic solvents and mineral oil.

ANIONIC SURFACE ACTIVE AGENTS may be expected to be wetting agents rather than detergents when the hydrophilic group is at or near the middle of a hydrophobic chain. The surface active agents are then considered to be oriented at the air-water interface as folded molecules with the hydrophilic group directed downward into the aqueous phase; a structure which in a series of compounds of the same chain length may lead to lower surface and interfacial tension, smaller micelles and higher critical micelle concentration. Sodium heptadecyl 9-sulfate (5) and the branched chain secondary alkyl sulfates (13) and sodium alkyl sulfosuccinates (1), which are important commercial wetting agents, have this relation between the hydrophilic and hydrophobic portions of the molecule.

In a previous report (12) it has been shown that sodium α-sulfopelargonic acid displays little evidence of surface active properties but becomes an efficient wetting agent upon esterification with n-octanol to form sodium octyl α-sulfopelargonate,

$$CH_3(CH_2)_6CH(SO_3Na)CO_2(CH_2)_7CH_3,$$

a compound with the hydrophilic portion at about the middle of the molecule and with hydrophobic alkyl groups of about equal chain length.

The present report concerns the preparation of a series of sodium alkyl α-sulfopelargonates and an investigation of properties, particularly in terms of the structure associated with best wetting characteristics. Further study of these and related esters is projected.

Synthesis

The individual normal primary, secondary, and branched chain primary alcohols of Table I were of standard laboratory quality, rectified by distillation as required. The "oxo" decyl alcohol (Enjay Chemical Co.) is a product from the oxo process, a mixture of 10 carbon atom primary alcohols, predominantly trimethylheptanols. The fluoro alcohol (E. I. du Pont de Nemours & Co., Inc.) is a technical product from the free radical telomerization of tetrafluoroethylene with methanol; the subscript 3 is an average number.

The esters of Table I were conveniently prepared by the same general method, esterification of sodium α-sulfopelargonic acid with a 10% excess of the particular alcohol, in the presence of sulfuric acid as the catalyst, and toluene to remove water of esterification, azeotropically. The following example illustrates the method. Analyses for Na and S agreed with

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TABLE I

Properties of Sodium Alkyl α-Sulfopelargonates

$C_7H_{15}CH(SO_3Na)CO_2R$

Alcohol ROH	Surface and interfacial tension, 0.2%, 25° dynes/cm.		Critical micelle concentration[a] millimoles/l.	Wetting time[b] 25°,0.1%, seconds		Ca^{++} *stability*[c] ppm	Foam height[d] 60°, 0.25%, mm.		Detergency[e] 60°, 0.25% distilled water, ΔR
	S.T.	I.T.		Distilled water	300 ppm		Distilled water	300 ppm	
C_2H_5OH	52.9	39.8	98.0	>300.0	>300.0	>1800	4	0	10
$C_5H_{11}OH$	40.3	18.9	16.0	12.1	5.3	310	80	140	15
$C_6H_{13}OH$	26.8	7.1	7.0	2.2	1.4	290	210	240	23
$C_7H_{15}OH$	26.6	5.7	4.5	0.0	4.7	440	210	240	26
$C_8H_{17}OH$	25.7	4.5	2.1	1.3	13.2	500	230	220	31
$C_6H_{13}CHOHCH_3$	26.4	4.8	3.6	1.3	4.5	520	220	230	25
$C_4H_9CH(C_2H_5)CH_2OH$	25.9	3.9	1.9	0.0	4.5	530	240	175	17
$C_9H_{19}OH$	25.4	3.8	1.2	3.8	33.1	500	230	80	31
$C_{10}H_{21}OH$	25.0	3.0	0.5	6.0	105.0	610	240	30	21
"Oxo"decyl	23.6	1.7	0.5	1.6	34.8	310	250	30	19
$C_{12}H_{25}OH$	25.2	1.0	0.1	103.0	>300.0	750	210	20	33
$H(CF_2CF_2)_3CH_2OH$	19.1	5.6	2.4	3.6	24.8	350	265	30	20
Sodium methyl α-sulfopalmitate	39.0	9.7	0.4	25.0	15.5	>1800	205	225	31

[a] Pinacyaole chloride method (2).

[b] Draves test, 5-g. skein, 3-g. hook (3).

[c] Modified Hart method (13).

[d] Ross-Miles (9) immediate foam height.

[e] Launder-Ometer,[3] 1 swatch of G.D.C. No. 26[3] (4) standard soiled cotton/100 ml./jar, 30 steel balls, 30 min., 2 replicates. ΔR = increase in reflectance after washing. ΔR for sodium dodecyl sulfate = 28.

the calculated values, with an average deviation of 0.15%.

Sodium Nonyl α-Sulfopelargonate. A stirred mixture of 0.1 mole of sodium α-sulfopelargonic acid, 0.11 mole of n-nonanol, 200 ml. of toluene and 2 ml. of concentrated sulfuric acid was refluxed 4 hrs. with azeotropic removal of water of esterification. The reaction mixture was neutralized with aqueous sodium carbonate and evaporated with recovery of toluene and excess nonanol. Ethanol was added to the residue, insoluble inorganic salts were removed, and the product was crystallized from 50% ethanol at−20°C. to give sodium nonyl α-sulfopelargonate as a white powder in a yield of 70%. Analysis: calculated for $C_{18}H_{35}NaO_5S$, 5.95% Na, 8.30% S; found 5.82% Na, 8.24% S.

Properties

In Table I comparison of the properties of sodium octyl, capryl, and 2-ethylhexyl α-sulfopelargonate with sodium methyl α-sulfopalmitate, all containing 17 carbon atoms, shows that the position of the hydrophilic portion at about the middle of the molecule results in lower surface and interfacial tension, higher c.m.c., and excellent wetting properties, but a somewhat lower calcium stability.

Surface and Interfacial Tension. In the pelargonate series surface tension measured at 0.2% concentration with the duNoüy tensiometer falls rapidly from the ethyl to the amyl to the hexyl ester and thereafter remains substantially the same except for the low value shown by the dodecafluoroheptyl ester.

The interfacial tension falls consistently with increase in molecular weight except for the values shown by the esters of secondary and branched chain alcohols and the dodecafluoroheptyl ester.

Critical Micelle Concentration. The c.m.c. was measured by the pinacyanole dye titration method (2), and is quite high for those esters which are not very surface active. Sodium ethyl α-sulfopelargonate in particular is hardly a surface active agent, has high surface and interfacial tension, high c.m.c., and practically no wetting, foaming, or detergent properties. The c.m.c. values for the surface active agents of the normal primary alcohols from amyl to dodecyl alcohol demonstrate a regularity and follow the relation $\text{c.m.c.} = \frac{(\text{c.m.c.})'}{2^N} = \frac{16}{2^N}$ (6,7,8) so that the found value agrees with the predicted. In the following list the predicted value is obtained by dividing 16 (the value for sodium amyl α-sulfopelargonate) by 2^N where N is the increase in the number of carbon atoms in going from the amyl ester to higher homologs:

Sodium n-alkyl α-sulfopelargonate	Critical micelle concentration, millimoles/l.	
	Found	Predicted
Amyl	16.0	......
Hexyl	7.0	8.0
Heptyl	4.5	4.0
Octyl	2.1	2.0
Nonyl	1.2	1.0
Decyl	0.5	0.5
Dodecyl	0.1	0.125

Wetting Time. Wetting properties of 0.1% solutions in distilled water and hard water of 300 p.p.m. were measured by the Draves test (3) using a 5-g. cotton skein and 3-g. hook, at 25°C. All of the pelargonate esters, except the ethyl and dodecyl, have wetting times of 6 sec. or less, either in distilled water or hard water.

The amyl ester has better wetting properties in hard water. The most efficient wetting agents are about equally effective in hard or soft water. The higher molecular weight esters (the nonyl, decyl, "oxo"decyl, and dodecafluoroheptyl esters) are more efficient in soft than in hard water.

The four most efficient wetting agents in both hard and soft water are the hexyl, heptyl, capryl, and 2-ethylhexyl esters. Branching of the alcohol portion, either by use of a branched chain primary alcohol or a normal secondary alcohol, improves solubility and wetting properties. This is evident with the capryl, 2-ethylhexyl, and "oxo"decyl esters.

Wetting time as a function of concentration is shown in Table II and Fig. 1. From this, it is appar-

TABLE II

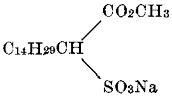
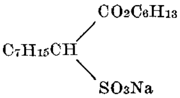
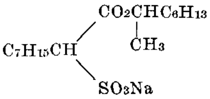
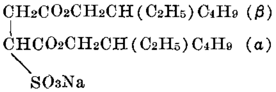
Wetting Time and Concentration

Sodium alkyl α-sulfopelargonate $C_7H_{15}CH(SO_3Na)CO_2R$	Wetting time, seconds, Draves test,[a] at various % concentrations in distilled water, 25°				
Alcohol, ROH	0.025	0.050	0.075	0.100	0.150
Amyl	......	......	30.5	12.1	4.4
Hexyl	80.2	12.3	5.2	2.2	0.0
Heptyl	10.2	2.8	1.7	0.0	......
Octyl	13.2	5.0	2.6	1.3	0.0
Capryl[b]	9.6	3.7	2.2	1.3	......
2-Ethylhexyl	10.5	2.7	1.5	0.0	......
Nonyl	25.9	8.8	5.5	3.8	2.3
Decyl	56.3	24.8	14.1	6.0	4.1

[a] Reference (3), 5-g. skein, 3-g. hook.

[b] $CH_3CHOHC_6H_{13}$.

TABLE III
Rate Constants, Acid and Alkaline Hydrolysis

Surface active agent	N/3 H_2SO_4, 100°		N/10 NaOH, 100°	
	k_1[a] min.$^{-1}$	Relative rate	k_2[b] l./mole/ min.	Relative rate
Sodium methyl α-sulfo-palmitate  $C_{14}H_{29}CH(CO_2CH_3)(SO_3Na)$	0.0047	30	0.14	60
Sodium hexyl α-sulfo-pelargonate  $C_7H_{15}CH(CO_2C_6H_{13})(SO_3Na)$	0.0020	13	0.16	18
Sodium capryl α-sulfo-pelargonate  $C_7H_{15}CH(CO_2CH(CH_3)C_6H_{13})(SO_3Na)$	0.0010	6	0.0092	1
Sodium di(2-ethylhexyl) sulfosuccinate  $CH_2CO_2CH_2CH(C_2H_5)C_4H_9$ (β) $CH(SO_3Na)CO_2CH_2CH(C_2H_5)C_4H_9$ (α)	0.0156 0.0033	100 21	0.9 approx.	100

[a] k_1 (first order) $= 1/t \ln \frac{a}{a - x}$

[b] k_2 (second order) $= 1/t \frac{x}{a(a - x)}$

ent that in the sodium n-alkyl α-sulfopelargonate series the heptyl ester,

$$CH_3(CH_2)_6CH(SO_3Na)CO_2(CH_2)_6CH_3,$$

with an equal number of carbon atoms in each alkyl group, is the most efficient wetting agent.

Calcium Stability, Foam Height, and Detergency. The calcium stability of the pelargonate esters, excluding the ethyl and dodecyl, ranges from about 300–600 p.p.m. indicating the esters are sensitive to hard water in some degree.

The esters all have good foaming properties in soft water, excepting the ethyl and amyl esters. The hexyl, heptyl, octyl, and capryl esters also have good foaming properties in hard water. The foam is stable and foam height remains about the same for 5 min. or more.

Surface active agents which are excellent wetting agents are not generally expected to have exceptional detergent properties. The pelargonate esters have moderately good detergency in soft water but are poor detergents in hard water in the absence of builders.

Stability to Hydrolysis. The sodium alkyl α-sulfopalmitates and stearates (10), and disodium 2-sulfoethyl α-sulfopalmitate (11) have been shown to resist hydrolysis, probably because the adjacent sulfo group protects the carboxylate linkage through steric hindrance. Esters of secondary alcohols are particularly stable to both acid and alkaline hydrolysis. The pelargonates of Table I are likewise stable to hydrolysis, as shown in Tables III and IV and Fig. 2.

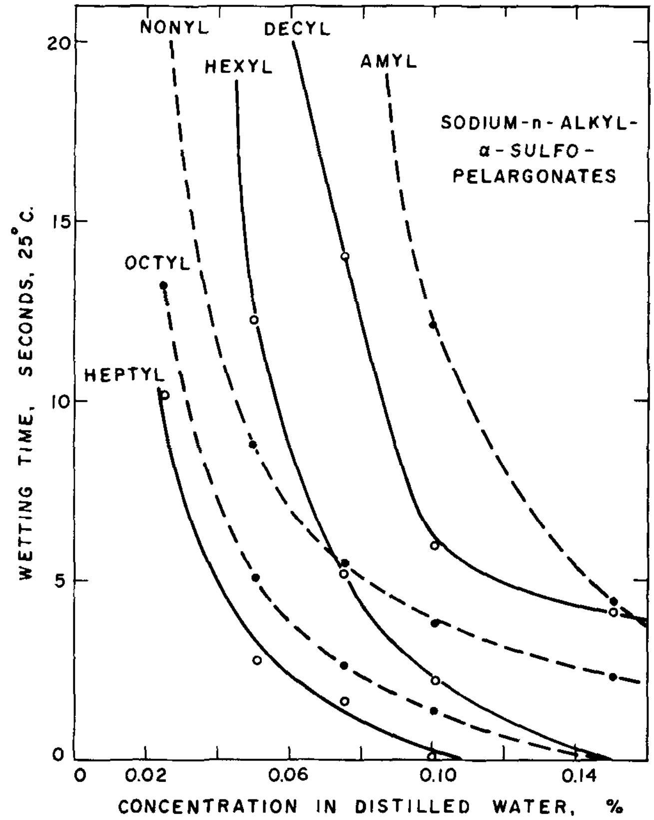


FIG. 1. Wetting properties of sodium n-alkyl α-sulfopelargonates.

Experiments to measure the rate constant for a first order acid catalyzed hydrolysis were carried out by heating 0.01 equivalent of the ester in 100 ml. of N/3 H_2SO_4 at 100°C., withdrawing 10-ml. aliquots for titration at selected intervals. Under these conditions, sodium di(2-ethylhexyl) sulfosuccinate appears to hydrolyze stepwise, first at the linkage unprotected by the sulfo group (β, k_1 0.0156) and then less rapidly at the ester linkage adjacent to the sulfo group (α, k_1 0.0033). The change from an initial rapid rate to a slower rate with a slope comparable to that for sodium hexyl α-sulfopelargonate is apparent in Fig. 2.

The rate constants for the second order alkaline hydrolysis were obtained in a similar manner, using an equivalent amount of 0.1 *N* NaOH. The value for sodium di(2-ethylhexyl) sulfosuccinate is an approximation at the midpoint; alkaline hydrolysis at 100°C. was too rapid to determine the rate for the first step in hydrolysis. Relative rates of hydrolysis and values for k_1 and k_2 are shown in Table III. Sodium capryl

TABLE IV
Stability to Hydrolysis, Wetting Properties in Acid and Alkali

Surface active agent	Wetting time, seconds, Draves test,[a] 0.1% concentration, 25°						
	Distilled water	5% H_2SO_4	After boiling in 5% H_2SO_4		1% NaOH	After boiling in 1% NaOH	
			for ½ hr.	for 1 hr.		for ½ hr.	for 1 hr.
Sodium methyl α-sulfopalmitate	25.0	28.2	36.8	36.5	36.8	>600.0	......
Sodium capryl [b] α-sulfopelargonate	1.3	3.5	5.8	6.6	4.4	8.0	21.2
Sodium heptyl α-sulfopelargonate	0.0	3.0	4.1	4.5	3.4	>600.0	......

[a] Reference (3), 5-g. skein, 3-g. hook.

[b] $CH_3CHOHC_6H_{13}$.

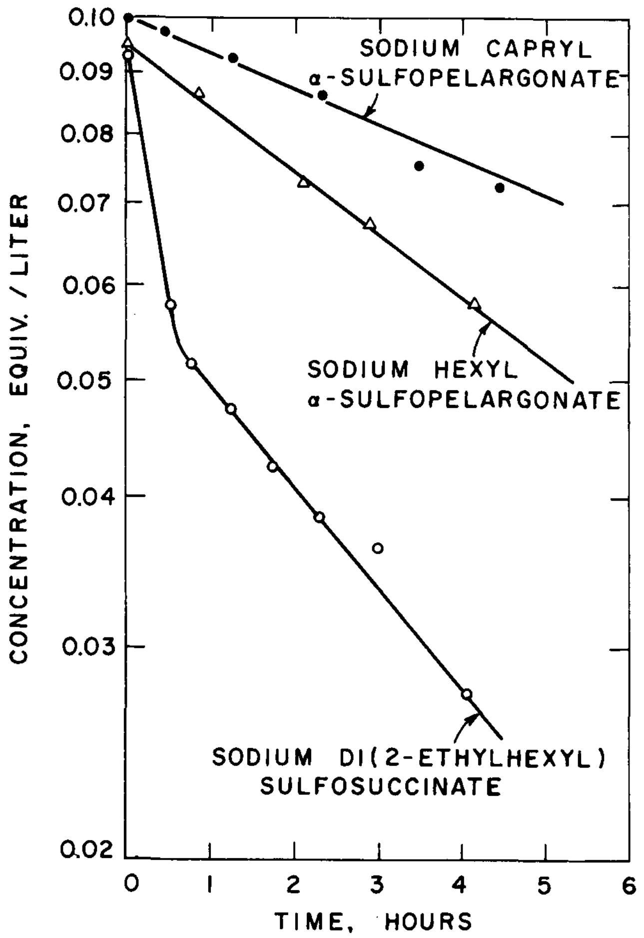


FIG. 2. Acid catalyzed hydrolysis of wetting agents.

α-sulfopelargonate, an ester of a secondary school, is quite resistant both to acid and alkaline hydrolysis. Differences in the stability of esters are further shown in Table IV. Sodium methyl α-sulfopalmitate has moderate wetting properties which are not destroyed by boiling in 5% H_2SO_4 but are destroyed by boiling in 1% NaOH. Sodium heptyl α-sulfopelargonate has excellent wetting properties in neutral or hot acid solution, but wetting properties are likewise destroyed through hydrolysis in hot alkaline solution. The wetting properties of the capryl ester persist in hot acid and alkaline solution.

Solubility. The sodium alkyl α-sulfopelargonates are easily soluble in water, and also surprisingly soluble in organic solvents and mineral oil. At 25°C. the amyl, hexyl, and 2-ethylhexyl esters are soluble to the extent of 10% or more in absolute ethanol, chloroform, ether, and petroleum ether, and soluble to the extent of about 1% in mineral oil.

Acknowledgment

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Lysine, Gossypol, and Nitrogen Solubility in Chemically Treated Cottonseed Meals

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The effects of treatment of commercial prepress-solvent extracted and direct-solvent extracted cottonseed marcs with several chemical agents and solvents were studied. The analytical results for "free" and "total" gossypol of the finished meals show that treatment with aliphatic amines, followed by extraction with a suitable solvent, removed large proportions of the "free" as well as "bound" gossypol. This reduction of "free" and "bound" gossypol was accompanied, in some experiments, by an increase in the nitrogen solubility and available lysine, as compared with the results obtained with the untreated air-dried marcs. The available lysine contents of the treated marcs was significantly correlated with the nitrogen solubility in 0.02 *N* aqueous NaOH.

THE NUTRITIVE QUALITY of cottonseed meals for nonruminant animals depends chiefly on the available lysine (lysine with the *epsilon* amino groups free) content of the meals. The available lysine in cottonseed is reduced during the processing of the seed for oil by (a) the actual destruction of lysine (1,2) and (b) by the addition of gossypol to the seed protein through the formation of a Schiff base with the *epsilon* amino groups of lysine. The present study was undertaken to determine the effect of treatment of defatted cottonseed meats with chemicals on the gossypol and available lysine contents of the treated meal.

Experimental

Commercial prepress-solvent extracted and direct-solvent extracted marcs were used as the sources of material for laboratory treatment with chemicals.

The experimental treatments of the marcs, which consisted of defatted cottonseed flaked meats still damp with adhering commercial hexane, were made

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[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.